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Ionizing Radiation and Antioxidants Affect Volatile Sulfur Compounds, Lipid Oxidation, and Color of Ready-to-Eat Turkey Bologna

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Bologna was processed from ground turkey breast meats containing one of four antioxidant treatments (none, rosemary extract, sodium erythorbate, and sodium nitrite). After it was cooked, the bologna was sliced, sealed in gas impermeable bags, exposed to 0, 1.5, and 3.0 kGy γ-radiation, and then stored at 5 °C for up to 8 weeks. Thiobarbuturic acid reactive substances (TBARS), color, and volatile sulfur compounds were measured every 2 weeks during storage. Irradiation had no consistent effect on TBARS values. The rosemary extract and sodium nitrite inhibited, while erythorbate increased, TBARS values, independent of radiation dose or storage time. Irradiation promoted redness and reduced yellowness of the control (no antioxidant) bologna at weeks 0 and 2. The use of nitrite and rosemary extract inhibited the changes in color due to irradiation. Several volatile sulfur compounds (hydrogen sulfide, methanethiol, methyl sulfide, and dimethyl disulfide), measured using a pulsed flame photometric detector, increased with radiation dose. However, none of the antioxidants had any substantial effect on volatile sulfur compounds induced by irradiation. Our results suggest that antioxidants did not consistently affect irradiation-induced volatile sulfur compounds of turkey bologna although they did significantly impact color and lipid oxidation.

KEYWORDS: Ionizing radiation; antioxidant; volatile sulfur compounds; bologna; lipid oxidation; color

INTRODUCTION

Ionizing radiation inactivates foodborne pathogens and extends the shelf life of raw meat and processed meat products. However, irradiation can induce the development of an off-odor at high doses for certain products. The off-odor has been described as wet dog, sulfur, metallic, burnt, or barbecued cornlike (*1*, *2*). It is believed that volatile sulfur compounds, not volatiles from lipids, are mostly responsible for the off-odor (*1*, *3*). Irradiation at 5 and 10 kGy increased the production of methyl sulfide (MS), dimethyl disulfide (DMDS), and dimethyl trisulfide (DMTS) in raw pork meat, but the increase was not dose-dependent (*1*). Fan et al. (*4*) showed that irradiation, in a dose-dependent fashion, increased the formation of hydrogen sulfide (H_2S), methanethiol (MT), MS, DMDS, and DMTS in cooked turkey breast. These sulfur compounds have very low odor thresholds (sub-ppb or ppt levels) and possess pungent, unpleasant aromas (*5*).

Antioxidants are commonly used by meat processors to retard the process of lipid oxidation. Nam et al. (*6*) showed that the addition of antioxidants such as tocopherol, gallic acid, and sesamol reduced the production of some volatile sulfur compounds in raw pork homogenates and patties. However, none of the above antioxidants is effective in reducing volatile sulfur compounds in turkey sausages (*7*). The effect of many other antioxidants on the production of sulfur compounds in ready-to-eat cooked meat products is largely unknown. Natural antioxidants such as rosemary extract (RM) have gained in popularity due to concerns over safety and toxicity of synthetic antioxidants. Rosemary or its extract has been used in many types of foods and model systems (*8*−*10*). RM has been shown to inhibit the formation of H_2S in ground pork meat due to high-temperature treatment (*11*). The addition of rosemary powder to linoleic acid reduces radiolysis of the fatty acid due to irradiation (*12*). Nitrite is commonly used in cured meat for color enhancement and for the prevention of toxin production by *Clostridium botulinum* (*13*). Another antioxidant, sodium erythorbate (NaEr), is used to prevent discoloration and the formation of nitrosamines (*14*).

The off-odor induced by irradiation may be more of a concern for ready-to-eat meats than raw meats because ready-to-eat meats are routinely consumed without further preparation. Turkey muscle is the most sensitive animal meat to irradiation in terms of off-flavor development (*15*). The objective of this study is to investigate the effects of selective antioxidants (RM, NaEr, and sodium nitrate) on irradiation-induced volatile sulfur compounds, lipid oxidation, and color changes of ready-to-eat turkey bologna.

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MATERIALS AND METHODS

Chemicals. All chemicals used for the manufacture of bologna were either reagent or food grade. Sodium tripoly-phosphate and NaEr were purchased from Spectrum Chemical Mtg. Corp. (Gardena, CA). Sodium chloride and sodium nitrite (NaNi) were from Aldrich (Milwaukee, WI). The RM (type HT-O) was provided by Kalsec Inc. (Kalamazoo, MI). Volatile sulfur compounds were purchased from Aldrich.

Bologna Manufacture. Ground turkey breast (10 kg) purchased from a local butcher was emulsified in a Hobart model HCM40 Cutter-Mixer (Hobart MFG Inc., Troy, OH) with the following ingredients (w/w per kg meat): 1% sodium chloride, 0.5% sodium tripoly-phosphate, 1% dextrose, and 20% deionized water. The above mixture was divided into four batches. To 2.5 kg batches were added 10 mL of vegetable oil (control), NaNi (final concentration, 200 mg/kg) plus 10 mL of vegetable oil, NaEr (final concentration, 500 mg/kg) plus 10 mL of vegetable oil, and RM in 10 mL of vegetable oil (final concentration, 0.075%). The amounts of NaNi and NaEr used in this study are the maximum permeable concentrations in cured meats (*14*). The batches were mixed for 5 min in a bowl mixer (model KSMC50S, KitchenAid Inc., Greenville, OH) to ensure uniform distribution of the added antioxidants. The emulsion was then stuffed into 2.5″ fibrous casings (Dewied Int., Santa Fe, NM) and cooked in a Koch model KL-50 Smokehouse (Koch Inc., Kansas City, MO) to an internal product temperature of 65.5 °C. After the internal temperature was reached, the meats were chilled using a sterile cold water bath. The bologna was sliced to a thickness of 4 mm (approximate) and placed into gas impermeable B-131-H foil bags (Bell Fiber Products Corp., Columbus, GA). Each bag contained five slices of bologna, and each slice weighed approximately 10 g. The bags were vacuum-packaged to 4 mmHg using a Multivac C-450 Vacuum Packager (Kansas City, MO) and stored overnight at 5 °C before irradiation. There were four replicates per treatment. The treatments were done independently and conducted at different days.

Irradiation and Dosimetry. Irradiation was conducted using a self-contained, Lockheed Corporation ^{137}Cs γ-radiation source (Marietta, GA). The source strength at the time of this study was ca. 98 600 Ci with a dose rate of 0.095 kGy min^{-1}. The temperature (4 °C) in the radiation chamber was maintained by introducing the vapor phase of liquid nitrogen into the radiation chamber. The targeted doses were 0, 1.5, and 3.0 kGy. The actual doses were within 5% of the target doses. A detailed description on irradiation and dosimetry has been reported (*1*).

Storage. After irradiation, the samples were stored at 5 °C for up to 8 weeks. At 2 week intervals, sulfur volatile compounds, lipid oxidation, and color were measured.

Extraction of Volatile Sulfur Compounds. Volatile sulfur compounds were extracted using a solid phase microextraction (SPME) method and analyzed using a gas chromatograph (GC) equipped with a pulse flame photometric detector (PFPD). The vials containing 10 g of chopped sample were incubated at 35 °C for 30 min on the Multicblock Heater (Lab Line Instruments, Melrose Park, IL) before the SPME fiber was inserted into the vials. An 85 μm StableFlex carboxen/poly(dimethylsiloxane) (Supelco, Bellefonte, PA) was the SPME fiber used in this study. Only one fiber was used in the entire experiment to eliminate variation caused by the individual fibers. The fiber was initially conditioned at 280 °C for 0.5 h. To extract volatile sulfur compounds from the samples, the stainless steel needle in which the fiber was housed was pierced through the vial septum. Once inside the vial, the fiber was pushed out of the housing and exposed to the headspace above the meat sample for 25 min at 35 °C. Then, the fiber was pulled back into the housing and the SPME device was removed from the vial and immediately inserted into the injection port of a GC system for thermal desorption at 240 °C for 5 min.

Separation and Identification of Volatile Sulfur Compounds. Volatile compounds were separated with an Agilent 6890 GC (Agilent Technologies, Palo Alto, CA) equipped with a GS-GasPro column (9.5 m × 0.32 mm i.d.) operated in the splitless mode and detected using the PFPD (OI Analytical, College Station, TX) at optimized sulfur detection conditions. A specially designed 0.8 mm SPME injector liner (Supelco) was used to prevent peak broadening. The temperature of the GC oven was set at 50 °C for 5 min and increased to 250 °C at 12.5 °C min^{-1} and held for 4 min at the final temperature. The injector and detector were operated at 240 and 260 °C, respectively. Helium was the carrier gas with a linear flow rate of 36.4 cm s^{-1}. The PFPD was operated in the sulfur mode with a 2 mm combuster sleeve and a B-12 filter. The voltage of the R1925 photomultiplier tube was 450 V. The signal collection gate was from 6 to 24 ms, and the trigger level was 100 mV. The ignitor current was 2.8 A. A model 5380 detector controller was used to collect signals and manually control gas flow to the PFPD. The gas flow rate to the detector was set to be 11.5 mL min^{-1} for hydrogen, 10 mL min^{-1} for air 1, and 15 mL min^{-1} for air 2. Fine adjustment of flows was made to optimize the sulfur signal. The detector signal and operation of the detector were facilitated by the use of the WinPulse software package (OI Analytical). The range was set at 10 during the entire run except between 7.1 and 8.5 min and between 10 and 11 min when the range was increased to 100. Compounds were identified by comparison of retention time of the sample compounds with those of standards. Because we could not establish standard curves for the volatile compounds due to the complexity of the matrix and the instability of the standards, the amounts of the sulfur compounds are presented as square roots of the peak area as the sulfur response of PFPD is pure quadratic (*16*).

Lipid Oxidation. Lipid oxidation was measured using the thiobarbituric acid (TBA) assay modified from the methods of Hodges et al. (*17*) and Zipser and Watts (*18*). Bologna samples (10 g) were homogenized with 20 mL of 0.5 M phosphate (pH 2.5) buffer containing 0.08% sulfanilamide and 0.01% BHT using a homogenizer (Virtishear, Virtis, Gardiner, NY) at a speed setting of 70 for 1 min. The homogenate was centrifuged at 12 000*g* for 10 min at 5 °C in a Sorvall RC2-B refrigerated centrifuge (Kendro Laboratory Products, Newtown, CT). The supernatant was then filtered through a Whatman 113V paper filter (Whatman, Clifton, NJ). A 1.6 mL filtrate was added to a test tube containing 1.6 mL of either (i) − TBA solution, 15% (w/v) trichloroacetic acid, or (ii) + TBA solution, containing the above plus 0.65% TBA. Samples were then mixed vigorously, heated at 95 °C in a water bath for 25 min, cooled, and centrifuged at 1300*g* for 10 min at 23 °C. The supernatant was filtered through a Millipore HV microfilter (Billerica, MA). Absorbances at 440, 532, and 600 nm were monitored using a Shimadzu UV-1601 spectrophotometer (Shimadzu Scientific Instruments, Columbia, MD). TBA reactive substance (TBARS) values are expressed as malondialdehyde (MDA) equivalent and calculated using the formulas developed by Hodges et al. (*17*).

Color Measurement. The color analysis was performed using a Hunter Miniscan XE meter (Hunter Laboratory, Inc., Reston, VA) (*19*). The meter was calibrated using black and white standard tiles. Illuminate D65, 10° standard observer, and a 2.5 cm port/viewing area were used. Four readings of *L*, *a*, and *b* values were taken per replicate, and there were 16 readings per treatment. *L* values indicate lightness, *a* values indicate greenness-redness, and *b* values indicate blueness-yellowness.

Statistical Analysis. There were four replicates in each treatment. A replicate of samples contained five slices of bologna in a bag. Multiple irradiation runs were carried out on the same day (each replicate of samples was irradiated separately). Measurements were made on the same days for all four replicates. Data were subjected to statistical analysis using SAS software (SAS Institute Inc., Cary, NC). The effects of radiation dose, antioxidant, and storage time were analyzed using the least significant difference test.

RESULTS

Lipid Oxidation. Antioxidant treatments had a profound effect on TBARS values in both irradiated and nonirradiated bologna (**Figure 1**). As compared with the control (no antioxidant) bologna, bologna that contained erythorbate had generally higher TBARS values while those containing nitrite and RM had lower TBARS values, regardless of radiation dose or storage time. Bologna containing RM had the lowest TBARS values. The effect of the antioxidants on TBARS values was independent of irradiation, reflecting the effectiveness of the antioxidants in controlling lipid oxidation prior to irradiation.

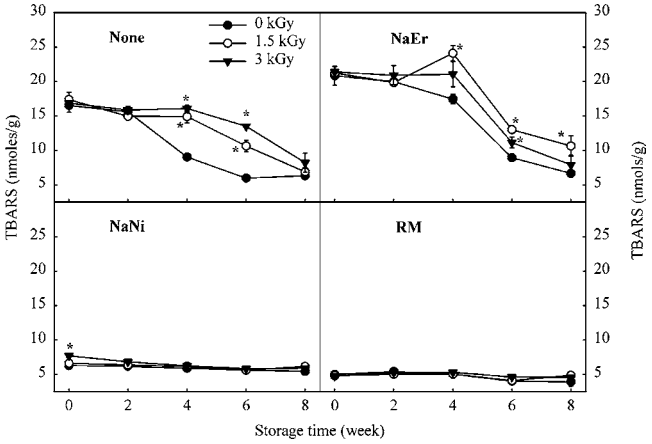

Figure 1. Effect of antioxidants, radiation dose, and storage on lipid oxidation of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. Lipid oxidation was measured as TBARS value (nmol/g) every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

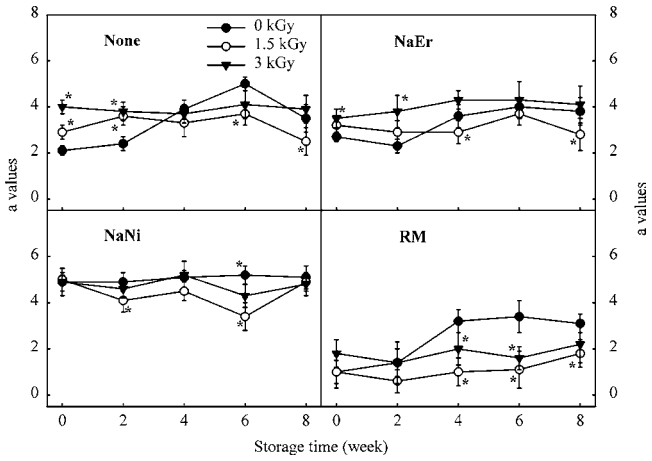

Figure 2. Effect of antioxidants and radiation dose on color (*a* values) of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. Color was measured every 2 weeks. Vertical bars represent standard errors ($n = 16$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

At week 0, TBARS values of all samples, regardless of antioxidant treatments, were not significantly ($P > 0.05$) affected by irradiation except that nitrite-containing bologna irradiated at 3 kGy had higher TBARS values than corresponding samples irradiated at 0 and 1.5 kGy (**Figure 1**). TBARS values of control bologna and those containing erythorbate generally decreased during storage. At weeks 4, 6, and 8, TBARS values of irradiated turkey bologna tended to be higher than those of nonirradiated samples in controls (no antioxidant) and bologna that contained erythorbate. During the entire storage (2−8 weeks), irradiation had no effect on TBARS values of the samples containing nitrite and rosemary.

Color. Regardless of radiation doses, samples containing nitrite had higher *a* values while those containing RM had lower *a* values than the controls (**Figure 2**), indicating that samples containing nitrite were redder (pinker) than controls while those with RM had the lowest redness prior to irradiation.

Irradiation increased the *a* values in control (no antioxidant) bologna and to a lesser extent in samples containing erythorbate as measured on the day of irradiation. The use of nitrite and RM completely reduced the increase in *a* values due to irradiation. *b* Values (yellowness) decreased with higher radiation doses (data not shown). Only nitrite was able to completely reduce the radiation-induced changes in *b* values (yellowness). The samples containing nitrite already had the lowest *b* values and the highest *a* values before irradiation.

Although irradiation increased the darkness and redness while yellowness was reduced in bologna measured on the day of irradiation in some samples, the effect of irradiation on color disappeared or reversed during storage. The samples containing RM that received radiation had lower *a* values than the corresponding nonirradiated samples after 4, 6, and 8 weeks of storage (**Figure 2**). The instrumental color measurements indicate that irradiation can induce redness in some turkey bologna but was not persistent during storage. It is unclear whether consumers could distinguish the color changes due to irradiation.

Volatile Sulfur Compounds. Volatile sulfur compounds were identified by comparing retention times with authentic compounds prepared in water. These compounds included H_2S, MT, carbon disulfide (CS_2), MS, DMDS, and DMTS (**Figure 3**). Our previous study on cooked turkey breasts using different SPME fibers and capillary GC columns revealed virtually the same volatile sulfur compounds (*4*). Several other minor peaks were also present in some irradiated samples but were not identified.

H_2S levels increased with radiation dose (**Figure 4**). None of the antioxidants, however, was able to reduce the production of H_2S induced by irradiation. In fact, all of the antioxidants promoted irradiation-induced H_2S levels in the ready-to-eat turkey bologna. During storage, the H_2S levels decreased rapidly in all turkey bologna types. After 6 weeks of storage, the levels become undetectable for control bologna and those containing nitrite. For bologna containing erythorbate, the irradiation-induced increase in the H_2S levels was observed during the entire storage period. CS_2 levels were not affected by irradiation or by antioxidant treatments (data not shown) and had no consistent changes during storage for any of the samples.

MT levels increased dramatically with higher radiation doses in all samples (**Figure 5**). None of the antioxidants reduced irradiation-induced MT production. MT levels of control bologna that was irradiated at 1.5 and 3.0 kGy decreased during storage. After 6 and 8 weeks of storage, control (no antioxidant) bologna that received 1.5 kGy of radiation had similar MT levels as the nonirradiated samples. However, bologna that received 3.0 kGy of radiation still had higher MT levels than the nonirradiated samples. In samples containing antioxidants, irradiated bologna always had higher MT levels than the nonirradiated samples during the 8 weeks of storage.

Although the initial MS levels were not significantly ($P > 0.05$) affected by irradiation at any dose regardless of antioxidant treatments (**Figure 6**), irradiated samples often had slightly higher MS levels than nonirradiated ones during storage in samples containing no antioxidant or erythorbate. In the samples containing nitrite or RM, MS levels of irradiated samples were lower than nonirradiated samples during the middle period of storage.

DMDS increased with higher radiation doses in all samples (**Figure 7**). The increased DMDS levels were observed during the entire 8 week storage period. During storage, DMDS slightly

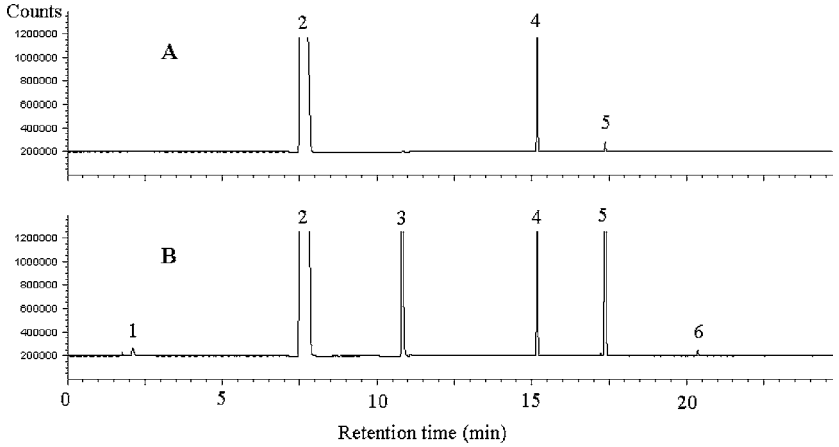

Figure 3. Sulfur compound profiles of nonirradiated turkey bologna (**A**) and those irradiated at 3 kGy (**B**). Measurements were made on the control (no antioxidant) bologna at week 0. The identified compounds are as follows: 1, H_2S; 2, CS_2; 3, MT; 4, MS; 5, DMDS; and 6, DMTS.

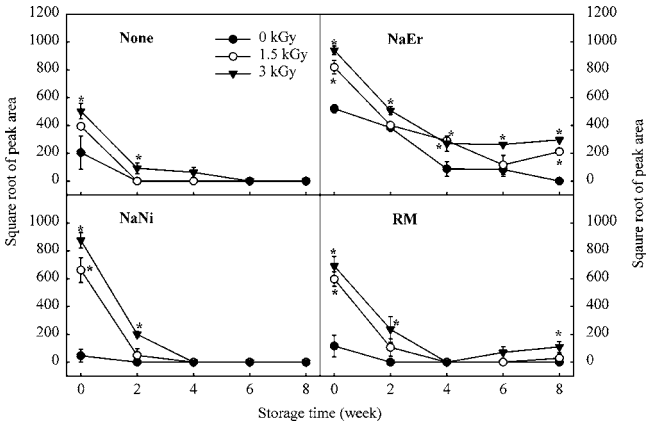

Figure 4. Effect of antioxidants and radiation dose on H_2S production of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. The volatile sulfur compound was measured every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

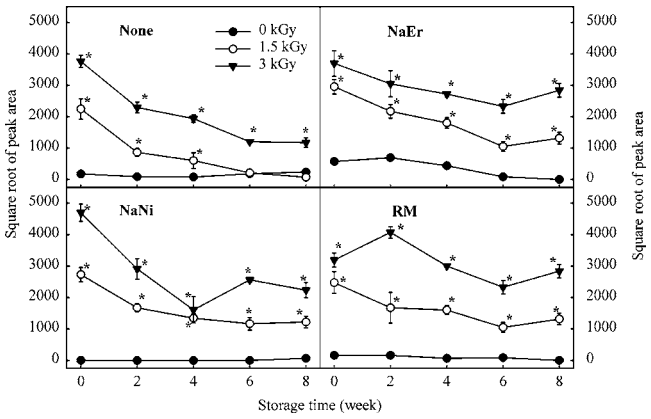

Figure 5. Effect of antioxidants and radiation dose on MT production of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. The volatile sulfur compound was measured every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

increased for most of the samples. None of the antioxidants had a consistent effect on the production of DMDS due to irradiation.

DMTS levels were not significantly ($P > 0.05$) affected by irradiation in control samples that contained no antioxidant during the entire storage period (**Figure 8**). However, irradiation increased DMTS levels in samples containing antioxidants as measured on the day of irradiation (week 0). During storage, irradiated bologna containing nitrite still had higher levels of DMTS than nonirradiated ones, while those containing erythorbate (or RM in some extent) had similar DMTS levels as the corresponding nonirradiated ones.

DISCUSSION

Erythorbate is a commonly used adjunct in cured meat for the reduction of nitrosomine formation. Shahidi et al. (*20*) tested a number of antioxidants on their effectiveness of lipid oxidation reduction in cooked ground pork. They found that erythorbic acid strongly inhibited lipid oxidation. Giroux et al. (*21*) demonstrated that the incorporation of ascorbic acid (0.03−0.5%) into beef patties before irradiation resulted in significant stabilization of the color parameters. Nam and others (*22*) showed that the addition of ascorbic acid at the 0.1% level to ground beef before irradiation effectively reduced the lipid oxidation and volatile sulfur compounds. Our results, however, suggest that erythorbate increased the lipid oxidation and H_2S levels and had no consistent effect on other volatile sulfur compounds or color. Ascorbic acid (an isomer of erythorbate) can serve as both an antioxidant and a prooxidant. Ascorbic acid induced the decomposition of lipid hydroperoxides (*23*). When a linoleic acid emulsion was exposed to ionizing radiation, 10 mM ascorbic acid exhibited prooxidant activity while concentrations of 100 and 500 mM ascorbic acid exerted antioxidant activity (*24*). Erythorbate, together with other ingredients, was added in meat samples prior to cooking. It is also possible that cooking and the interaction of eryhthorbate with food components or other ingredients altered the properties of erythorbate.

Nitrite has been used in cured meat products to stabilize meat color, to improve texture, to develop the characteristic cured meat flavor, and to eliminate microbial growth (*14*). Because of its high reactivity, nitrite reacts readily with food components, such as myoglobin. Lipid oxidation measured as TBARS values was reduced by adding nitrite before cooking, presumably due to the reaction of MDA with nitrite and nitrous acid (*25*). Our earlier study (*19*, *26*) suggested that irradiation induced lipid oxidation in beef frankfurters. Shahidi et al. (*27*) showed that

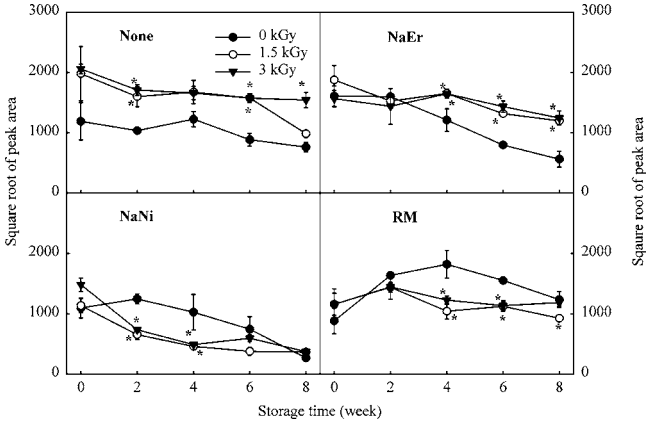

Figure 6. Effect of antioxidants and radiation dose on MS production of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. The volatile sulfur compound was measured every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

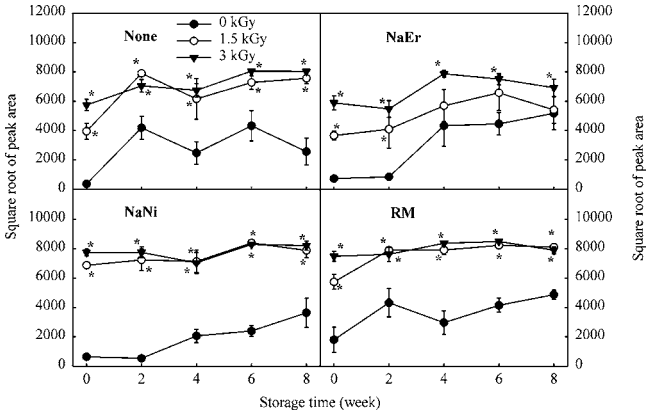

Figure 7. Effect of antioxidants and radiation dose on DMDS production of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. The volatile sulfur compound was measured every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

irradiation at 5 and 10 kGy has no detrimental effect on lipid oxidation in cured pork meat. In the present study, no consistent effect by irradiation on lipid oxidation was observed in the turkey bologna vacuum-packaged in air impermeable film bags, perhaps due to the low fat levels (<4%) of turkey bologna. Nitrite made the turkey bologna samples lighter, more red, and less yellow. Similar effects by nitrite on color have been observed in cured meat (*27*).

It has been shown that RM is a strong antioxidant in terms of reducing lipid oxidation in a number of meats (*8*, *28*). RM is a primary antioxidant, which can react with radicals to convert them to more stable products. The application of RM after cooking resulted in lower lipid oxidation as opposed to applications before cooking (*29*). Du and Ahn (*7*) showed that rosemary is the weakest antioxidant among the tested antioxidants including tocopherol, gallic acid, and sesamol in turkey sausages. The addition of RM (0.03%) in pork frankfurters had no effect on TBARS values (*9*). Our results showed that RM applied before cooking acted as a strong antioxidant against lipid oxidation but reduced the redness of turkey bologna.

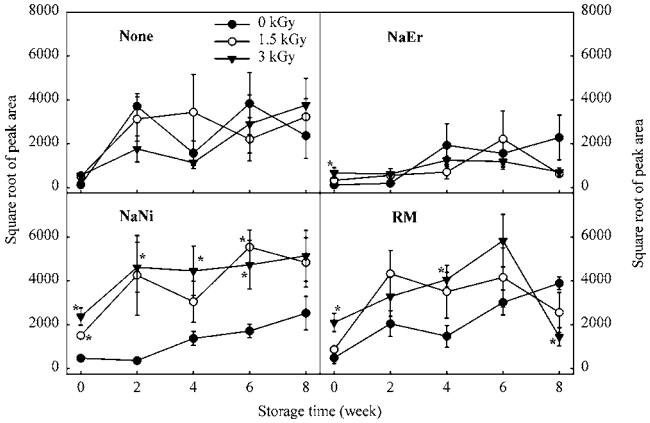

Figure 8. Effect of antioxidants and radiation dose on DMTS production of ready-to-eat turkey bologna. Sliced bologna made from ground turkey breast containing no antioxidant (none), NaEr, NaNi, and RM was γ-irradiated at 0, 1.5, and 3.0 kGy and then stored at 5 °C for 8 weeks. The volatile sulfur compound was measured every 2 weeks. Vertical bars represent standard errors ($n = 4$). An asterisk indicates a significant ($P < 0.05$) difference from the nonirradiated samples.

The present study suggests that irradiation increased the production of all sulfur compounds except CS_2, similar to our earlier study on cooked turkey breast (*4*). Among the sulfur compounds induced by irradiation, MT increased the most (a 20-fold increase as compared to nonirradiated controls). MT has one of the lowest odor thresholds among volatile sulfur compounds (*5*). Our results also suggested that the use of antioxidants did not consistently affect irradiation-induced sulfur compounds in the ready-to-eat meat. Earlier studies showed that sesamol, gallic acid, and Trolox alone or in combinations reduced the production of TBARS and volatile sulfur compounds in pork patties (*6*) and turkey breast homogenates (*30*). In another study, Lee and others (*31*) showed that the antioxidants had no effect on the production of volatile sulfur compounds, color change, or off-odor intensity of irradiated turkey breast meat but that the addition of sesamol + tocopherol or gallate + tocopherol was effective in reducing TBARS values of turkey breast meat, especially under aerobic conditions. Du and Ahn (*7*), however, showed that none of the antioxidants influenced the development of off-odor volatile compounds in turkey sausage. It appears that the effect of antioxidants on the irradiation-induced volatile sulfur compounds differs in cooked meat products as compared to raw meats. In the present study, antioxidants were added to a raw meat mixture, followed by cooking and irradiation. The antioxidant capacity may have been diminished as a result of the cooking process prior to irradiation. It is known that nitrite decreases rapidly to levels below the analytical detection limit during the curing process (*13*).

It seems that the mechanism for production of volatile sulfur compounds is different from lipid oxidation in response to irradiation and antioxidants. For example, antioxidants such as RM significantly inhibited lipid oxidation but did not consistently influence volatile sulfur compounds in control samples (no antioxidant). Irradiation promoted the production of volatile sulfur compounds, not lipid oxidation. Although free radicals may be involved in both lipid oxidation and formation of sulfur compounds in foods, their mechanisms may differ. The direct reaction of lipids is a free radical chain reaction involving the reaction of singlet oxygen with unsaturated lipids and formation of hydroxyperoxides, which further go through propagation and termination steps. The primary mechanism of irradiation effects in foods containing mostly water is the generation of free

radicals as a result of water radiolysis. These radicals include hydrated electrons, hydroxyl radicals, and hydrogen atoms. These primary radicals then react with food components. It is not completely clear how sulfur compounds are produced, although it is believed that volatile sulfur compounds are synthesized from amino acids either as free forms or as protein components (*32*, *33*). New strategies to reduce volatile sulfur compounds have to be explored. Antioxidants have to be present prior to irradiation and be in the proximity of proteins or amino acids to protect against the attack of radicals on sulfur-containing amino acids.

Irradiation inactivated microorganisms and reduced the population of microflora in the bologna samples. The growth of microflora in the bologna during storage may impact color, lipid oxidation, and formation of volatile sulfur compounds. After 8 weeks of storage, the total plate counts in nonirradiated bologna were significantly higher ($P < 0.05$) than the irradiated samples, regardless of antioxidant treatments (data not shown). The differential growth of microorganisms could partially be responsible for the changes in color and lipid oxidation during storage and for the differences in color, lipid oxidation, and volatile sulfur compounds between irradiated and nonirradiated samples after prolonged (6 and 8 weeks) storage.

In summary, RM and nitrite inhibited lipid oxidation while erythorbate promoted lipid oxidation in both irradiated and nonirradiated bologna. Irradiation increased the redness and reduced the yellowness of bologna. The use of RM and erythorbate in the meat emulsion prevented the color changes due to irradiation. Irradiation significantly increased the production of several volatile sulfur compounds. None of the antioxidants had a consistent effect on the formation of sulfur compounds due to irradiation.

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LITERATURE CITED

(1) Ahn, D. U.; Jo, C.; Du, M.; Olson, D. G.; Nam, K. C. Quality characteristics of pork patties irradiated and stored in different packaging and storage conditions. *Meat Sci*. **2000**, *56*, 203−209.

(2) Huber, W.; Brasch, A.; Waly, A. Effect of processing conditions on organoleptic changes in foodstuffs sterilized with high-intensity electrons. *Food Technol*. **1953**, *7*, 109−115.

(3) Pearson, A. M.; Costilow, R. N.; Batzer, O. F.; Sliwinski, R. A.; Chang, L. Relation between panel scores and certain chemical components in precooked irradiated meats. *Food Res.* **1959**, *24*, 228−234.

(4) Fan, X.; Sommers, C. H.; Thayer, D. W.; Lehotay, S. J. Volatile sulfur compounds in irradiated precooked turkey breast analyzed with pulsed flame photometric detection. *J. Agric. Food Chem*. **2002**, *50*, 4257−4261.

(5) Shankarananarayana, M. L. R. B.; Abraham, K. O.; Natarajan, C. P. Volatile sulfur compounds in food flavors. *CRC Crit. Rev. Food Sci. Nutr*. **1973**, *4*, 395−435.

(6) Nam, K. C.; Prusa, K. J.; Ahn, D. U. Addition of antioxidant to improve quality and sensory characteristics of irradiated pork patties. *J. Food Sci.* **2002**, *67*, 2625−2630.

(7) Du, M.; Ahn, D. U. Effect of antioxidants on the quality of irradiated sausages prepared with turkey thigh meat. *Poult. Sci*. **2002**, *81*, 1251−1256.

(8) Barbut, S.; Josephson, D. B.; Maurer, A. J. Antioxidant properties of rosemary oleoresin in turkey sausage. *J. Food Sci.* **1985**, *50*, 1356−1359, 1363.

(9) Coronado, S. A.; Trout, G. R.; Dunshea, F. R., Shah, N. P. Antioxidant effects of rosemary extract and whey powder on the oxidative stability of wiener sausages during 10 months frozen storage. *Meat Sci*. **2002**, *62*, 217−224.

(10) Karpinska, M.; Borowski, J.; Danowska-Oziewicz, M. Antioxidative activity of rosemary extract in lipid fraction of minced meat balls during storage in a freezer. *Nahrung* **2000**, *44*, 38−41.

(11) Langourieux, S.; Escher, F. E. Sulfurous off-flavor formation and lipid oxidation in heat-sterilized meat in trays. *J. Food Sci.* **1998**, *63*, 716−720.

(12) Lacroix, M.; Smoragiewicz, W.; Pazdernik, L.; Kone, M. I.; Krzystyniak, K. Prevention of lipid radiolysis by natural antioxidants from rosemary (*Rosmarinus officinalis* L.) and thyme (*Thymus vulgaris* L.). *Food Res. Int*. **1997**, *30*, 457−462.

(13) Anonymous. Nitrate, nitrite, and nitroso compounds in foods. *Food Technol*. **1987**, *4*, 127−134.

(14) Madhavi, D. L.; Singhal, R. S.; Kulkarni, P. R. Technical aspects of food antioxidants. In *Food Antioxidants. Technological, Toxicological and Health Perspectives*; Madhavi, D. L., Deshpande, S. S., Salunkhe, D. K., Eds.; Marcel Dekker: New York, 1995; pp 159−265.

(15) Sudarmadji, S.; Urbain, W. M. Flavor sensitivity of selected animal protein foods to gamma radiation. *J. Food Sci.* **1972**, *37*, 671−672.

(16) Amirav, A.; Jing, H. Pulsed flame photometric detector for gas chromatography. *Anal. Chem*. **1995**, *67*, 3305−3318.

(17) Hodges, D. M.; DeLong, J. M.; Forney, C. F.; Prange, R K. Improving the thiobarbituric acid-reactive substances assay for estimating lipid peroxidation in plant tissues containing anthocyanin and other interfering compounds. *Planta* **1999**, *207*, 604−611.

(18) Zipser, M. W.; Watts, B. M. A modified 2-thiobarbituric acid (TBA) method for the determination of malondialdehyde in cured meats. *Food Technol*. **1962**, *16* (7), 102−104.

(19) Sommers, C. H.; Fan, X. Antioxidant power, lipid oxidation, color, and viability of *Listeria monocytogenes* in beef bologna treated with gamma radiation and containing various levels of glucose. *J. Food Prot*. **2002**, *65*, 1750−1755.

(20) Shahidi, F.; Rubin, L. J.; Wood, D. F. Control of lipid oxidation in cooked ground pork with antioxidant and dinitrosyl ferrohemochrome. *J. Food Sci.* **1987**, *52*, 564−567.

(21) Giroux, M.; Ouattara, B.; Yefsah, R.; Smoragiewicz, W.; Saucier, L.; Lacroix, M. Combined effect of ascorbic acid and gamma irradiation on microbial and sensorial characteristics of beef patties during refrigerated storage. *J. Agric. Food Chem*. **2001**, *49*, 919−925.

(22) Nam, K. C.; Min, B. R.; Park, K. S.; Lee, S. C.; Ahn, D. U. Effects of ascorbic acid and antioxidants on the lipid oxidation and volatiles of irradiated ground beef. *J. Food Sci*. **2003**, *68*, 1680−1685.

(23) Lee, S. H.; Oe, T.; Blair, I. A. Vitamin C-induced decomposition of lipid hydroperoxides to endogenous genotoxins. *Science* **2001**, *292*, 2083−2086.

(24) Wong, P. Y. Y.; Kitts, D. D. Factors influencing ultraviolet and electron beam irradiation-induced free radical free radical damage of ascorbic acid. *Food Chem*. **2001**, *74*, 75−84.

(25) Kolodziejska, I.; Skonieczny, S.; Rubin, L. J. Malondialdehyde-nitrite interactions in meat and model systems. *J. Food Sci.* **1990**, *55*, 925−928, 946.

(26) Sommers, C. H.; Fan, X. Gamma irradiation of fine-emulsion sausage containing sodium diacetate. *J. Food Prot*. **2003**, *66*, 819−824.

(27) Shahidi, F.; Pegg, R. B.; Shamsuzzaman, K. Color and oxidative stability of nitrite-free cured meat after gamma irradiation. *J. Food Sci*. **1991**, *56*, 1450−1452.

(28) Wu, T. W.; Lee, M. H.; Ho, C. T.; Chang, S. S. Elucidation of the chemical structures of natural antioxidants isolated from rosemary. *J. Am. Oil Chem. Soc*. **1982**, *59*, 339−345.

(29) Guntensperger, B.; Hammerli-Meier, D. E.; Escher, F. E. Rosemary extract and precooking effects on lipid oxidation in heat-sterilized meat. *J. Food Sci*. **1998**, *63*, 955−957.
(30) Lee, E. J.; Ahn, D. U. Effect of antioxidants on the production of off-odor volatiles and lipid oxidation in irradiated turkey breast meat and meat homogenates. *J. Food Sci*. **2003**, *68*, 1631−1638.
(31) Lee, E. J.; Love, J.; Ahn, D. U. Effect of antioxidants on consumer acceptance of irradiated turkey meat. *J. Food Sci*. **2003**, *68*, 1659−1663.
(32) Jo, C.; Ahn, D. U. Production of volatile compounds form irradiated oil emulsion containing amino acids and proteins. *J. Food Sci*. **2000**, *65*, 612−616.
(33) Stewart, E. M. Food irradiation chemistry. In *Food Irradiation: Principles and Applications*; Molins, R. A., Ed.; John Wiley and Sons: New York, 2001; pp 37−69.

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